Research Article | DOI:10.5281/zenodo.7465017
www.jnanosam.com

NANOSAM
Journal of NanoScience in Advanced Materials

Magnetic and Magnetocaloric Properties of $_{0.5}Pr_{0.67}Ba_{0.22}Sr_{0.11}Mn_{0.95}Fe_{0.05}O_3/_{0.5}Pr_{0.67}Ba_{0.22}Sr_{0.11}Mn_{0.9}Fe_{0.1}O_3$ Composite

Khaled Snini[1] and Mohamed Ellouze[1#]

In the present work, the magnetic and magnetocaloric properties of $_{0.5}Pr_{0.67}Ba_{0.22}Sr_{0.11}Mn_{0.95}Fe_{0.05}O_3$ /$_{0.5}Pr_{0.67}Ba_{0.22}Sr_{0.11}Mn_{0.9}Fe_{0.1}O_3$ (0.5PBSMF$_{0.05}$/0.5PBSMF$_{0.1}$) composite have been investigated. Our composite 0.5PBSMF$_{0.05}$/0.5PBSMF$_{0.1}$ has been synthesized using the solid–state reaction. X-ray diffraction (XRD) at room temperature has been used to carry out the structural properties. In order to investigate the magnetic and magnetocaloric properties of the samples, magnetization measurements dependence on temperature and magnetic field have been performed by using physical property measurement system. XRD results indicate that all our simples crystallized in the orthorhombic structure with Pnma space group. Magnetization measurements versus temperature for the composite reveal two magnetic transition temperatures associated to both manganites, which induces an enlargement of the magnetic entropy change peak. Based on Maxwell relation, the maximum magnetic entropy change ($|\Delta S_M^{max}|$) of the composite has been calculated as 1.18×10^{-3} Jkg^{-1}K^{-1}, which corresponds to relative cooling power (RCP) about 17.8 Jkg^{-1} under a magnetic field change of 5T.

1. Introduction

Perovskite manganites with the general formula $A_{1-x}B_xMnO_3$ (A = Pr, La, Nd,… and B = Ba, Sr, Ca,..) have been of large recent interest due to their electrical and magnetic properties [1-4]. This type of materials can be used in different technological applications such as colossal magneto-resistance, computer memory systems, storage devices and magnetic refrigerants [5-8]. The magnetic ground state in these materials is sensitive to variations of the Mn–O bond length and Mn–O–Mn bond angle and Mn^{3+}/ Mn^{4+} ions [9]. The variation of ions in A and B-sites has a sensitive impact on physical properties of perovskite manganites. Also, the Mn site substitution by different elements affects the Mn-O-Mn networks and the combination of the double-exchange interaction (DE) coupled Mn^{3+}/ Mn^{4+} ions [10, 11].

The reported magnetocaloric effect (MCE) in the manganites and the ability to control their Curie temperature by chemical substitutions opened doors for the production of new candidates of nonpolluting magnetic refrigerants in a wide temperature range. Also, MCE is becoming a promising technology to replace the conventional gas compression-expansion technique [12, 13]. The MCE can be defined as the adiabatic temperature change (ΔT_{ad}) or the isothermal magnetic entropy change (ΔS_M) of a system due to the applied magnetic field [14]. In addition, the manganites have attracted the widest interest in aspects of theoretical and experimental researches due to their large magnetic entropy change. More than that, a large magnetic entropy change can be tuned in a large temperature range, intervening on the chemical composition of these materials, which is advantageous for magnetic refrigeration [15, 16]. Moreover, the manganites are very convenient for the synthesis routes, and their Curie temperature can be justified under various doping conditions. Therefore, the new trends have been focusing on studying the MCE of manganite composites [17, 18].

In this work, we elaborated by the solid state method at high temperature, the composite $Pr_{0.67}Ba_{0.22}Sr_{0.11}Mn_{0.95}Fe_{0.05}O_3/Pr_{0.67}Ba_{0.22}Sr_{0.11}Mn_{0.9}Fe_{0.1}O_3$ composite studied their magnetic and magnetocaloric properties.

2. Results and Discussion

The powder X-ray diffraction (XRD) patterns of our samples have been recorded at room temperature. Figures 1a-b) show the refined XRD

[1]*University of Sfax, Faculty of Sciences of Sfax (FSS), LMEEM, km 3.5, B.P.1171, 3000 Sfax Tunisia.*
#Corresponding author: sninikhaled2@gmail.com

Keywords: Manganites; X-ray diffraction; Rietveld refinement; Magnetization; Relative cooling power.

Received: 21 November 2022 | Accepted: 19 December 2022 | Published: 25 December 2022

NANOSAM
Journal of NanoScience in Advanced Materials

patterns for $Pr_{0.67}Ba_{0.22}Sr_{0.11}Mn_{0.95}Fe_{0.05}O_3$/$Pr_{0.67}Ba_{0.22}Sr_{0.11}Mn_{0.9}Fe_{0.1}O_3$ samples, including the observed and calculated profiles as well as the difference profile. Our samples are single phase without any detectable impurity and crystallize in the orthorhombic system with a Pbnm space group [19]. After the formation of the two mother compounds, $Pr_{0.67}Ba_{0.22}Sr_{0.11}Mn_{0.95}Fe_{0.05}O_3$ /$Pr_{0.67}Ba_{0.22}Sr_{0.11}Mn_{0.9}Fe_{0.1}O_3$, we prepared the composite with composition 50% of each.

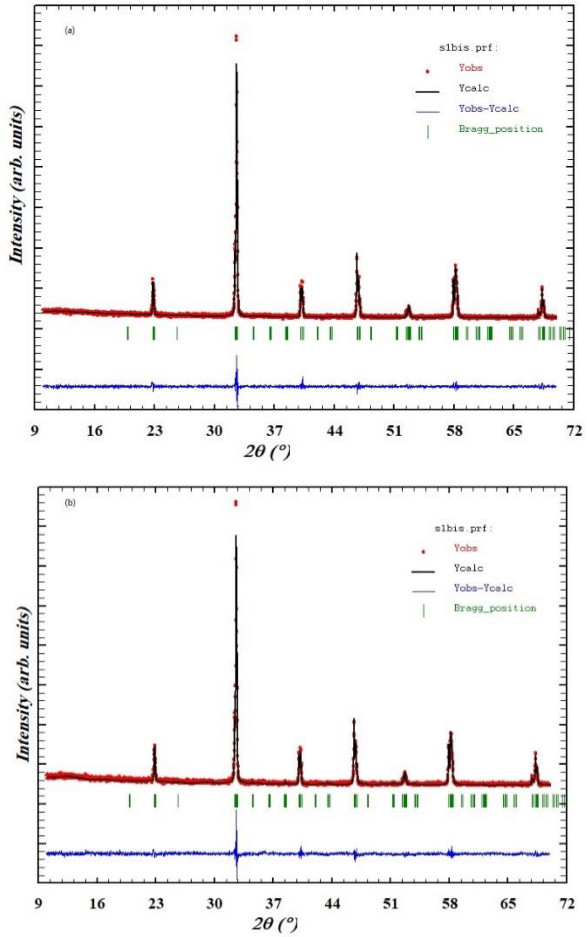

Figure 1. Observed and calculated X-ray diffraction data and Rietveld refinement for **a)** $Pr_{0.67}Ba_{0.22}Sr_{0.11}Mn_{0.95}Fe_{0.05}O_3$ and **b)** $Pr_{0.67}Ba_{0.22}Sr_{0.11}Mn_{0.9}Fe_{0.1}O_3$. Vertical bars are the Bragg reflections for the space group Pnma. The difference pattern between the observed data and fits is shown at the bottom.

Figure 2 shows the XRD patterns of $0.5Pr_{0.67}Ba_{0.22}Sr_{0.11}Mn_{0.95}Fe_{0.05}O_3/0.5Pr_{0.67}Ba_{0.22}Sr_{0.11}Mn_{0.9}Fe_{0.1}O_3$ composite. From the Fig. 2, we can notice the evolution of the most intense peak, which reflects a broadening signature of composite formation. These results are similar to those reported by *E. Sellami et al.* [22].

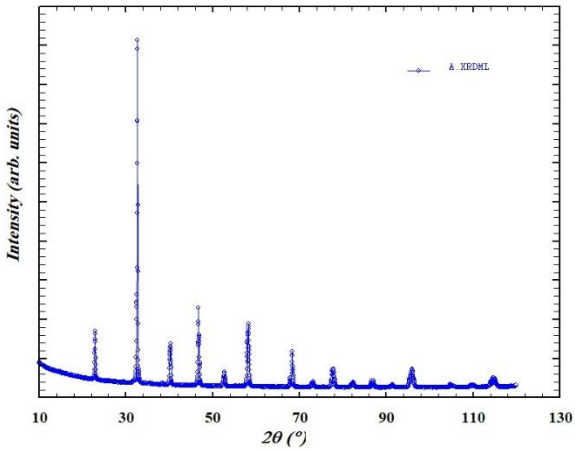

Figure 2. Refined X-ray powder diffraction for $0.5Pr_{0.67}Ba_{0.22}Sr_{0.11}Mn_{0.95}Fe_{0.05}O_3/0.5Pr_{0.67}Ba_{0.22}Sr_{0.11}Mn_{0.9}Fe_{0.1}O_3$ composite.

The magnetic properties of the $PBSMF_{0.05}$ and $PBSFM_{0.1}$ manganites and their composite were characterized by the magnetization measurement vs. temperature in the range 5–350 K under a magnetic applied field of 0.05T. Fig. 3a shows the temperature dependence of the magnetization M (T) for both parent compounds. We clearly observed a sharp transition from paramagnetic to ferromagnetic state with decreasing temperature. The Curie temperature T_C was determined from dM/dT plots shown in the inset of Fig. 3a. It is found to be 135K for PBSMF0.05 and 70 K for PBSFM0.1. The M(T) curves of the $0.5PBSMF_{0.05}/0.5PBSFM_{0.1}$ composite shown in Fig. 3b have two magnetic phase transitions which are in accordance with the $PBSMF_{0.05}$ and $PBSFM_{0.1}$ phase transition. At low temperatures when compared to the magnetization values of the $PBSMF_{0.05}$ and $PBSFM_{0.1}$ manganites, the magnetization value of the $0.5PBSMF_{0.05}/0.5PBSFM_{0.1}$ composite is smaller than that of individual phases. This decrease caused by interactions between different magnetic phases with different T_C [23].

The variation of the magnetization as a function of magnetic applied field up to 5T at several temperatures.was also measured for 0.5 PBSMF0.05 /0.5 PBSFM0.1 composites (Fig. 4). At low temperatures, the magnetization M increases sharply at low magnetic fields ($\mu_0H < 0.5$ T) and then saturates above 1 T. This result confirms the existence of ferromagnetic state at low temperatures for our composite.

In order to study the nature of magnetic phase transition, Banerjee criterion allows the determination of the order of the magnetic transition. It is based on the observation of the slope of the isotherm plots M^2 vs. μ_0H/M, a positive or a negative slope indicates a second order or first order transition, respectively [24]. The Arrott plots

NANOSAM
Journal of NanoScience in Advanced Materials

M^2 vs. $\mu_0 H/M$ for the studied of the composite is displayed in Fig. 5. The Arrott curves have a positive slope witch indicate that our composite undergoes a second order FM–PM phase transition.

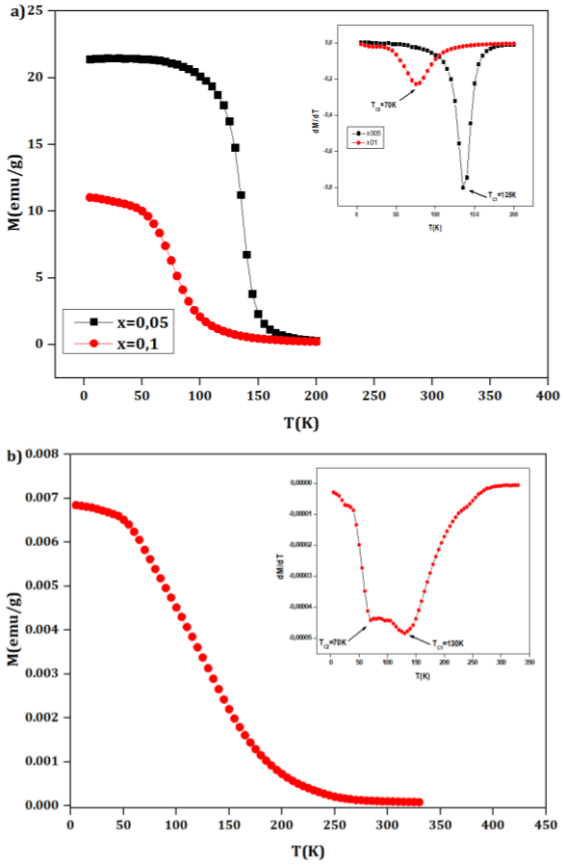

Figure 3. M(T) curves for **a)** $PBSMF_{0.05}$, $PBSFM_{0.1}$ manganites and **b)** their composite at μ0H = 0.05 T magnetic field. The inset is the dM/dT curves.

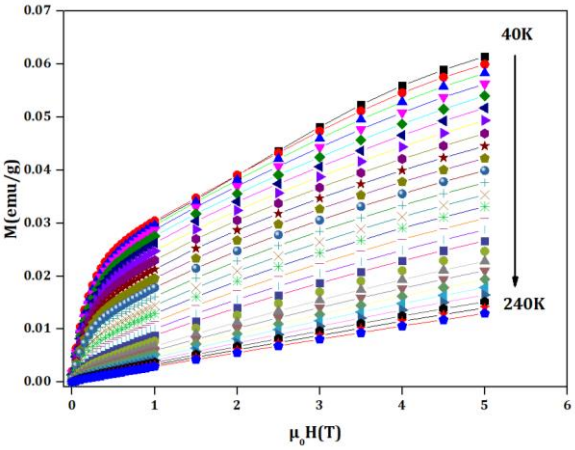

Figure 4. Isothermal magnetization for $0.5Pr_{0.67}Ba_{0.22}Sr_{0.11}Mn_{0.95}Fe_{0.05}O_3/0.5Pr_{0.67}Ba_{0.22}Sr_{0.11}Mn_{0.9}Fe_{0.1}O_3$ composite measured at several temperatures.

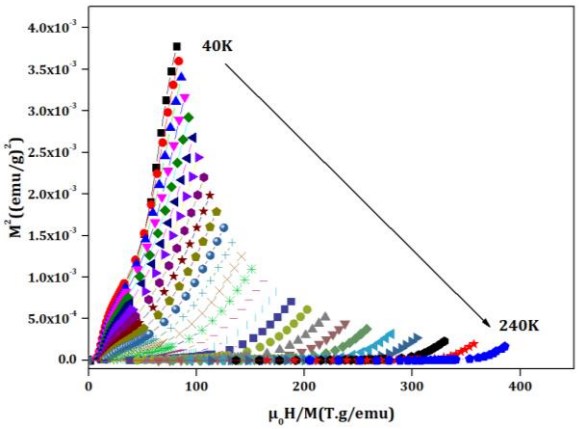

Figure 5. H/M vs. M^2 curves of isotherms for $0.5Pr_{0.67}Ba_{0.22}Sr_{0.11}Mn_{0.95}Fe_{0.05}O_3/0.5Pr_{0.67}Ba_{0.22}Sr_{0.11}Mn_{0.9}Fe_{0.1}O_3$ composite.

The magnetic entropy change (ΔS_M) of the 0.5 $PBSMF_{0.05}$ /0.5 $PBSFM_{0.1}$ composite, can be calculated from the isothermal magnetization measurements by applying to the formula given below [25]

$$|\Delta S_M| = \sum_i \frac{M_i - M_{i+1}}{T_{i+1} - T_i} \Delta H \qquad (1)$$

Where M_i and M_{i+1} are the values of magnetization measured at T_i and T_{i+1}, respectively.

Figure 6 shows $|\Delta S_M|$ as a function of temperature under different magnetic applied field variations for the 0.5 $PBSMF_{0.05}$ /0.5 $PBSFM_{0.1}$ composite. As expected, $|\Delta S_M|$ exhibits two maximums around the transition temperatures, and the maximum ΔS_M value, increases with the amplitude of the magnetic applied field change. Under a magnetic applied field change of 5 T, it amounts 1.18 10^{-3} J kg^{-1} K^{-1} for composite.

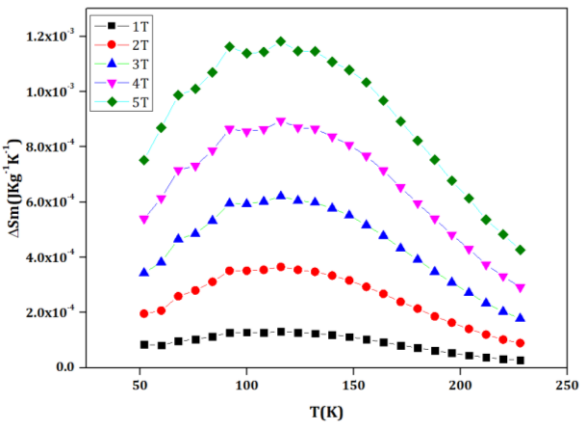

Figure 6. Temperature dependence of the magnetic entropy change $|\Delta S_M|$ for the composite at different applied magnetic field.

The relative cooling power (RCP) for our composite, which expresses the cooling power of the magnetocaloric material, is determined by the following expression [26]

$$RCP\ (S) = -\Delta {S_M}^{max} \times \delta T_{FWHM} \quad (2)$$

δT_{FWHM} is the full-width at half maximum of the curve of ΔS_M. Under a magnetic applied field of 5T, the obtained values of RCP are found to be 175, 122 and 17.8 J/Kg for the $PBSMF_{0.05}$, $PBSFM_{0.1}$ manganites and 0.5 $PBSMF_{0.05}$ /0.5 $PBSFM_{0.1}$ composite, respectively. The values display that RCP value of the composite is decreased by 10% when compared to those of $PBSMF_{0.05}$, $PBSFM_{0.1}$ manganites. The decrease of The RCP can be explained by the increase in the number ratio of Fe^{3+}-O-Fe^{3+} in the composite, which induces a weakening of the ferromagnetism. In addition, this evolution can be explained by the fact that the presence of iron weakens the double exchange interactions to the profit of the super exchange ones in the complex Fe^{3+}-O-Mn^{3+}[27-31]. We summarized in Table 1 the Curie temperature T_C, $-\Delta S_M^{max}$ and RCP values, in order to compare the results with those reported in literature [32-35].

Table 1. Comparison of magnetocaloric properties of our samples with the literature.

Materials	$\mu_0 H$ (T)	RCP (Jkg^{-1})	Ref.
$PBSMF_{0.05}$	5	175	This work
$PBSFM_{0.1}$	5	122	This work
0.5 $PBSMF_{0.05}$ /0.5 $PBSFM_{0.1}$	5	17.8	This work
$La_{0.67}Ca_{0.33}MnO_3/Fe_3O_4$	1	62.42	[32]
$(La_{0.7}Ca_{0.3}MnO_3)_{0.9}/(Co_3O_4)_{0.1}$	3	160	[33]
$0.9La_{0.6}Ba_{0.2}Sr_{0.2}MnO_3/_{0.1}Co_2O_3$	1	100.86	[34]
Gd	5	410	[35]

3. Conclusion

To conclude our scientific studies, the 0.5 $PBSMF_{0.05}$ /0.5 $PBSFM_{0.1}$ composite has been obtained by the mixture of the $PBSMF_{0.05}$ and $PBSFM_{0.1}$ samples in the mass ratio of 0.5:0.5 using the solid–state reaction. The magnetic and magnetocaloric properties have been studied by magnetization measurements. Magnetic measurements show that all samples exhibit a PM-FM transition with decreasing temperature. They exhibit a second-order ferromagnetic to paramagnetic phase transition. The magnetic phase transition of the materials has been determined as second order by using Banerjee criterion. The $-\Delta {S_M}^{max}$ and RCP value for the 0.5 $PBSMF_{0.05}$ /0.5 $PBSFM_{0.1}$ composite under 5 T magnetic fields have been calculated as 1.18 10^{-3} J $kg^{-1}K^{-1}$ and 17.8 J/ kg respectively. Therefore, we indicate that the obtained results will represent attention of research for the development of magnetic refrigeration devices

Method

First of all, two manganites powder with compositions of $Pr_{0.67}Ba_{0.22}Sr_{0.11}Mn_{0.95}Fe_{0.05}O_3$ / $Pr_{0.67}Ba_{0.22}Sr_{0.11}Mn_{0.9}Fe_{0.1}O_3$ were elaborated using the solid-solid method at high temperature. Synthesis method is reported elsewhere [19] using stoichiometric amounts with higher purity than 99.9% of Pr_6O_{11}, BaO_2, SrO_2, MnO_2 and Fe_2O_3. Then, the appropriate amount of both samples with 50% of each was mixed and a homogenous powder was pressed into pellets and sintered at 1200 °C for 12h. The obtained samples were characterized by powder X-ray diffraction at room temperature in Panalytical X'PERT Pro diffractometer, using $\theta/2\theta$ Bragg–Brentano geometry with diffracted beam monochromatized CuK_α radiation. The diffraction patterns were collected by steps of 0.017 over the angle range 10–70°. Structural analyses were checked by the Rietveld method using the FullProf program [20, 21]. Magnetization measurements were carried out using a vibrating sample magnetometer (VSM) operating between 40 and 240K with an applied magnetic field up to 5T. Magnetocaloric effect (MCE) was estimated based on the magnetization measurements versus magnetic applied field up to 5T at several temperatures.

Acknowledgements

This work was funded by the Ministry of Higher Education and Scientific Research, Tunisia. Award number: PRF2019-D4P2.

Authors' contributions

K.S: Experimental parts, structural analyses and contribute to writing the manuscript. M.E: magnetization measurement and contribute to writing part of the manuscript

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

NANOSAM
Journal of NanoScience in Advanced Materials

References

[1] Jin, S., Tiefel, T.H., McCormack, M., Fastnacht, R.A., Ramesh, R., Chen, L.H. "Thousandfold Change in Resistivity in Magnetoresistive La-Ca-Mn-O Films", Science **264**, 413–415 (1994).
[2] Zimm, C., Jastrab, A., Sternberg, A., Pecharsky, V.K., Gschneider Jr, K.A., Osbore, M., Anderson, I., "Magnetic properties and magnetic entropy change in spinels (Cd,M)Cr2S4 with M=Cu or Fe", Journal of Applied Physics **103**, 07B315 (2008).
[3] Gamzatov, AG., Aliev, AM., Batdalov, AB., Ahmadvand, H., Salamati, H., Kameli, P., "Specific heat and magnetocaloric effect of Pr1-xAgxMnO3", J Mater Sci **49**, 294–299 (2014).
[4] Abdel-Khalek, E.K., EL-Meligy, W.M., Mohamed, E.A., Amer, T.Z., Sallam. H.A., "Study of the relationship between electrical and magnetic properties and Jahn-Teller distortion in R(0.7)Ca(0.3)Mn(0.95)Fe(0.05)O(3) perovskites", J. Phys. Condens. Matter **21**, 026003 (2009).
[5]Thaljaoui, R., Boujelben, W., Pe¸kała, M., Pe¸kała, K., "Structural and electrical properties of monovalent doped manganites Pr0.6- Sr0.4-xKxMnO3 (x = 0, 0.05 and 0.1)". J Supercond Nov Magn **26**,1625–1630(2013).
[6] Coey, JMD., Viret, M., von Molnar, S., "Mixed-valence manganites". Adv Phys (48), 167–293(1999).
[7] Hong, S.C., Kim, S.J., Hahn, E.J., Park, S. l., Kim, C.S., "Magnetic Refrigeration Properties of La0.8Ca0.2Mn0.9957Fe0.01O3", IEEE Trans. Magn. **45**, (6) 2565 - 2568 (2009).
[8] Tishin, A.M., Spichkin, Y.I., "The magnetocaloric effect and its applications". Institute of Physics Publishing, Bristol (2003).
[9] Millis, AJ., Littlewood, PB., Shraiman, BI., "Double exchange alone does not explain the resistivity of La1-xSrxMnO3". Phys Rev Lett **74**, 5144–5147 (1995).
[10] Chang, Y. L., Huang, Q., Ong, C. K., J. "Effect of Fe doping on the magnetotransport properties in Nd0.67Sr0.33MnO3 manganese oxides", Appl. Phys. **91**, 789 (2002).
[11] Baazaoui, M., Zemni, S., Boudard, M., Rahmouni, H., Gasmi, A., Selmi, A., Oumezzine, M., "Magnetic and electrical behaviour of La0.67Ba0.33Mn1−xFexO3 perovskites", Mater. Lett. **63**, 2167-2170 (2009).
[12] Gschneidner, K. A., Pecharsky Jr, V. K., Tsokol, A. O., "Recent developments in magnetocaloric materials", Rep. Prog. Phys. **68**, 1479-1539 (2005).
[13] Tegus, O., Brück, E., Buschow, K .H .J., Boer, F. R., "Transition-metal-based magnetic refrigerants for room-temperature applications", Nature **415**, 150-152 (2002).
[14] Phan, M. H., Tian S. B., Hoang D. Q., Yu S. C., Nguyen C., and Ulyanov A.N., "Large magnetic-entropy change above 300K in CMR materials", Journal of Magnetism and Magnetic Materials **258-259** , 309–311 (2003).
[15] Ayadi, F., Regaieg, Y., Cheikhrouhou-Koubaa, W., Koubaa, M., Cheikhrouhou, A., Lecoq, H., Nowak, S., Ammara, S., Sicard, L., "Preparation of nanostructured La0.7Ca0.3− xBaxMnO3 ceramics by a combined sol–gel and spark plasma sintering route and resulting magnetocaloric properties". J. Magn. Magn. Mater **381**, 215-219 (2015).
[16] Mathews, S. P., Kaul, S. N., "Tuning magnetocaloric effect with nanocrystallite Size", Appl. Phys. Lett **98**, 172505 (2011).
[17] Akça, G., Kılıç Çetin, S., Ekicibil, A., "Magnetic and magnetocaloric properties of 0.5La0.7Ca0.2Sr0.1MnO3/0.5La0.7Te0.3MnO3 composite", J. Sci. Cumhuriyet., **41**, 144-151 (2020).
[18] Wang, G. F., Zhao, Z. R., Li, H .L., Zhang. X. F. "Enhancement of refrigeration capacity and table-like magnetocaloric effect in La0.8Ca0.2MnO3/ La0.8K0.2MnO3 nanocrystalline composite", J. Ceramics International, **41**, 9035-9040 (2015).
[19] Snini, K., Ben Jemaa, F., Ellouze, M., Hlil, E. K., "Structural, magnetic and magnetocaloric investigations in Pr0.67Ba0.22Sr0.11Mn1-xFexO3 (0 ≤ x ≤ 0.15) manganite oxide", J. Alloys Comp **739**, 948-954 (2018).
[20] Rietveld, H. M., "A profile refinement method for nuclear and magnetic structures", J. Appl. Cryst **2**, 65-71 (1969).
[21] Roisnel, T., Rodriguez-Carvajal. J, "Computer Program FULLPROF", LLB-LCSIM, May, (2003).
[22] Sellami-Jmal, E., Regaieg, Y., Cheikhrouhou-Koubaa, W., Koubaa, M., Cheikhrouhou, A., Njah, N., "Magnetic and Magnetocaloric Properties of La0. 65Ca0. 35MnO3/La0. 7Ca0. 2Ba0. 1MnO3 and La0. 65Ca0. 35MnO3/Pr0. 5Sr0. 5MnO3 Composite Manganites", J. Supercond Nov Magn **28**, 3121–3126 (2015).
[23] Romero-Muñiz, C., Franco, V., Conde, A., "Influence of magnetic interactions between phases on the magnetocaloric effect of composites", Appl. Phys. Lett **102 (2)**, 1-5 (2013)
[24] Banerjee, B. K., "On a generalised approach to first and second order magnetic transitions". Phys. Lett **12**, 16-17 (1964).
[25] Pecharsky, V.K., Gschneidner Jr, K.A., "Magnetocaloric effect and magnetic refrigeration", J. Magn. Magn. Mater **200**, 44-56 (1999).
[26] Gschneidner Jr, K. A., Pecharsky, V. K., "Magnetocaloric Materials", Annu. Rev. Mater. Sci. **30**, 387-429 (2000).
[27] Nasri, A., Hlil, E. K., Lehlooh, A. F., Ellouze, M., Elhalouani, F., "Study of magnetic transition and magnetic entropy changes of Pr0.6Sr0.4MnO3 and Pr0.6Sr0.4Mn0.9Fe0.1O3 compounds", Eur. Phys. J. Plus **131**, 110 (2016).
[28] Zouari, S., Kahn, M. L., Ellouze, M, Elhalouani, F., "Effect of iron substitution on the physico-chemical properties of Pr0.6La0.1Ba0.3Mn1−xFexO3 manganites (with 0 ≤ x ≤0.3)", Eur. Phys. J. Plus **130**, 177 (2015).
[29] Xianyu Wen-xu, Li Bao-he, Qian Zheng-nan, Jin Han-min, "Effect of Fe doping in $La_{1-x}Sr_xMnO_3$", J. Appl. Phys. **86**, 5164 (1999).
[30] Jian-Wang Cai, Cong Wang, Bao-Gen Shen, Jian-Gao Zhao, Wen-Shan Zhan, "Colossal magnetoresistance of spin-glass perovskite $La_{0.67}Ca_{0.33}Mn_{0.9}Fe_{0.1}O_3$", Appl. Phys. Lett **71**, 1727-1729 (1997).
[31] Sahasrabudhe, M. S., Patil, S. I., Date, S. K., Adhi, D. P., Kulkarni, S. D., Joy. P.A, Bathe. R.N, "Influence of magnetic (Fe^{+3}) and non-magnetic (Ga^{+3}) ion doping at Mn-site on the transport and magnetic properties of $La_{0.7}Ca_{0.3}MnO_3$", Solid State Commun **137**, 595-600. (2006).
[32] M'nassri, R., Cheikhrouhou, A., "Magnetocaloric effect in different impurity doped La0.67Ca0.33MnO3 composite". J. Supercond. Nov. Magn **27**, 421-425 (2014).
[33] Anwar, M.S., Ahmed, F., Danish, R., Koo, B.H., "Impact of Co3O4 phase on the magnetocaloric effect and magnetoresistance in La0.7Sr0.3MnO3/Co3O4 and La0.7Ca0.3MnO3/Co3O4 ceramic composites", Ceram. Int. **41**, 631-637 (2015).
[34] M'nassri, R., Chniba Boudjada, N., Cheikhrouhou, A., "Nearly constant magnetic entropy change involving the enhancement of refrigerant capacity in(La0.6Ba0.2Sr0.2MnO3)1−x/(Co2O3)x composite", Ceram. Int. **42**, 7447-7454 (2016) .
[35] Phan, M-H., Yu, S-C., "Review of the magnetocaloric effect in manganite materials", J. Magn. Magn. Mater **308**, 325-340 (2007).